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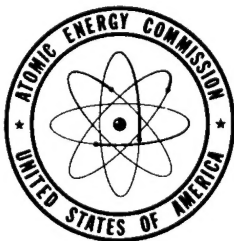
UNITED STATES ATOMIC ENERGY COMMISSION

THERMAL EXPANSION OF ZIRCONIUM AND ZIRCONIUM–TIN ALLOYS UP TO 570°C

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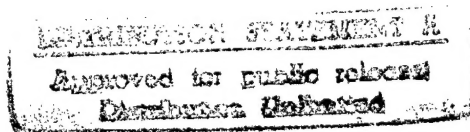
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I. INTRODUCTION

The present work was undertaken as part of the research being done in the design of a nuclear reactor for the Navy. Interest is centered on zirconium because of its low neutron absorption and high corrosion resistance, thus making it useful for cladding and various structural parts in a reactor. The addition of tin to zirconium, in proper amounts, produces an alloy with a higher resistance to corrosion than zirconium alone [1].

Various specimens of polycrystalline zirconium and zirconium-tin alloys were prepared for the purpose of obtaining useful engineering data on their thermal properties, specifically, thermal expansion.

From plots of length vs. temperature, as measured by a dial gauge mounted on an electric furnace and a thermocouple-potentiometer circuit, respectively, empirical equations of the second degree were derived by the method of least squares, one for each of the five samples of pressed and sintered zirconium and zirconium-tin powders. These equations represent the thermal linear expansion of the samples between 30° and 570°C and are of the form

$$L_t = L_o (1 + at + bt^2) \qquad (1)$$

where L_t is the length of the sample at any temperature, t, and L_o the length at 0°C; a and b are constants.

From equation (1) may be derived the instantaneous linear coefficient at any temperature within the experimental range as well as an average coefficient between two temperatures. By differentiating L_t once with respect to t and dividing by L_o, one obtains an instantaneous coefficient as follows:

$$\alpha_t = \frac{dL}{dt} \frac{1}{L_o} = a + 2 bt \qquad (2)$$

An estimation of relative error indicates that values of coefficients are correct to within 0.6%.

A comparison with the results of similar expansion work done on a sintered powder compact of pure zirconium shows agreement within 6% between values for the mean coefficient of expansion between 0 and 500°C. [2]

The relationship between tin content and linear coefficient at any temperature will be discussed in Part III.

II. EXPERIMENTAL

A. Materials

The samples were prepared from mixtures of -325 mesh, Grade C
sponge zirconium hydride powder, mechanically pulverized, and
-325 mesh metallic tin powder. They were pressed at 75 tsi
with a die lubricated with stearic acid and sintered 10 hours
at $1270^{\circ}C$ in vacuo. The dimensions of the bars thus formed
were roughly $1/3"$ x $1/3"$ x 5-$1/3"$; all five bars were then
machined down to cylindrical rods $4"$ long and $1/4"$ in diameter
with small protruding pins $3/16"$ long centered at each end to
facilitate mounting in the quartz tube holder.

B. Apparatus

Measurements were made with a standard quartz tube dilatometer
equipped with a dial gauge calibrated in ten-thousandths of an
inch. In operation, the specimen is seated and centered, by
means of the end pin, inside and at the bottom of a quartz tube
which is suspended inside an electric furnace and supported at
the top by a clamp attached to the exterior of the furnace.

Another quartz tube of the same outside diameter as the specimen
fits over the upper end of the specimen and extends upward and
slightly beyond the outer tube. Upon the top of this inner tube
rests the dial gauge. A chromel-alumel thermocouple resting in
a small transverse hole bored at the midpoint of the specimen and
led through the tubes to a potentiometer indicates specimen tem-
perature.

The reading limit of the dial gauge is $\pm$ $0.0001"$. Temperatures
may be determined to $\pm$ $1.5^{\circ}C$.

III. PROCEDURE AND RESULTS

The heating rate control of the furnace was set at approximately $2.5^{\circ}C$
per minute; the average cooling rate was appreciably lower. A constant
stream of argon was passed over the specimen during both heating and
cooling to avoid possible contamination. In spite of this, all the
specimens lost their silvery appearance and became quite darkened after
the first few runs. It is assumed that the data obtained were not
affected by this thin oxide layer.

Dial gauge and potentiometer readings were taken at approximately
50-degree intervals.

III. PROCEDURE AND RESULTS (Cont'd.)

Anywhere from two to six runs were made on each specimen, depending upon the repeatability of the length vs. temperature plot. Reasonable repeatability of the curves was achieved after what were assumed to be stresses due to machining were relieved by reheating. Cooling curves were disregarded, insofar as calculations were concerned, because of poor precision of the dilatometer during the cooling cycle as a result of a mechanical defect in the dial gauge.

The final heating curve for each sample was graphically corrected for the expansion of the quartz tube and used for a determination of a second degree equation —equation (2)—by the method of least squares. The equations thus derived apply in the temperature range between 30° and $570^\circ C$ and are listed in Table I.

Expansion curves for the various materials are given in Fig. 1. Values of $\Delta L/L_0$ were calculated directly from equation (1). By simple manipulation, this equation may be put into the required form.

$$L_t = L_0 + L_0 (at + bt^2)$$

$$\frac{L_t - L_0}{L_0} = at + bt^2$$

where

$$L_t - L_0 = \Delta L$$

Thus

$$\frac{\Delta L}{L_0} = at + bt^2 \qquad\qquad (3)$$

TABLE I

Composition of Sample	Equation
100% Zr, 0% Sn	$L_t = 4.0040\,(1 + 5.99 \times 10^{-6}t + 1.55 \times 10^{-9}t^2)$
99% Zr, 1% Sn	$L_t = 3.9986\,(1 + 5.98 \times 10^{-6}t + 1.86 \times 10^{-9}t^2)$
97% Zr, 3% Sn	$L_t = 3.9947\,(1 + 6.31 \times 10^{-6}t + 1.29 \times 10^{-9}t^2)$
95% Zr, 5% Sn	$L_t = 4.0058\,(1 + 6.04 \times 10^{-6}t + 2.62 \times 10^{-9}t^2)$
93% Zr, 7% Sn	$L_t = 3.9883\,(1 + 6.70 \times 10^{-6}t + 1.84 \times 10^{-9}t^2)$

L_t is expressed in inches if t is in degrees centigrade.

III. PROCEDURE AND RESULTS (Cont'd.)

The overall linear expansion per unit length increases with tin content over the temperature range studied, as may be seen from Fig. 1.

The variation of instantaneous coefficient with temperature is shown in Fig. 2. This is actually a plot of the slopes of the curves of Fig. 1 against temperature. As may be seen, the instantaneous coefficient does not always increase with tin content.

Metallographic analysis reveals the location of the tin-rich phase at the grain boundaries. Fig. 3 shows the five specimens under polarized light magnified 200x. The tin phase shows up as small white areas at the grain boundaries.

IV. CONCLUSIONS

The experimental data obtained from thermal linear expansion measurements on zirconium and zirconium-tin alloy specimens containing 0%, 1%, 3%, 5%, and 7% tin by weight were used to derive separate second degree equations for each specimen, relating length and temperature. On the basis of these equations the following conclusions may be drawn regarding the expansion coefficients:

1. The linear expansion coefficients increase with temperature for all the specimens tested.

2. The mean coefficients increase with tin content over the temperature range studied but the instantaneous coefficients do not show the same uniformity.

3. The data obtained for the 0% tin specimen agree within 6% with previously published data on a sintered powder compact of pure zirconium.

BIBLIOGRAPHY

(1) M. C. Udy, H. L. Shaw, F. W. Boulger, BMI-711, Battelle
    Memorial Institute, 1951, p. 67.
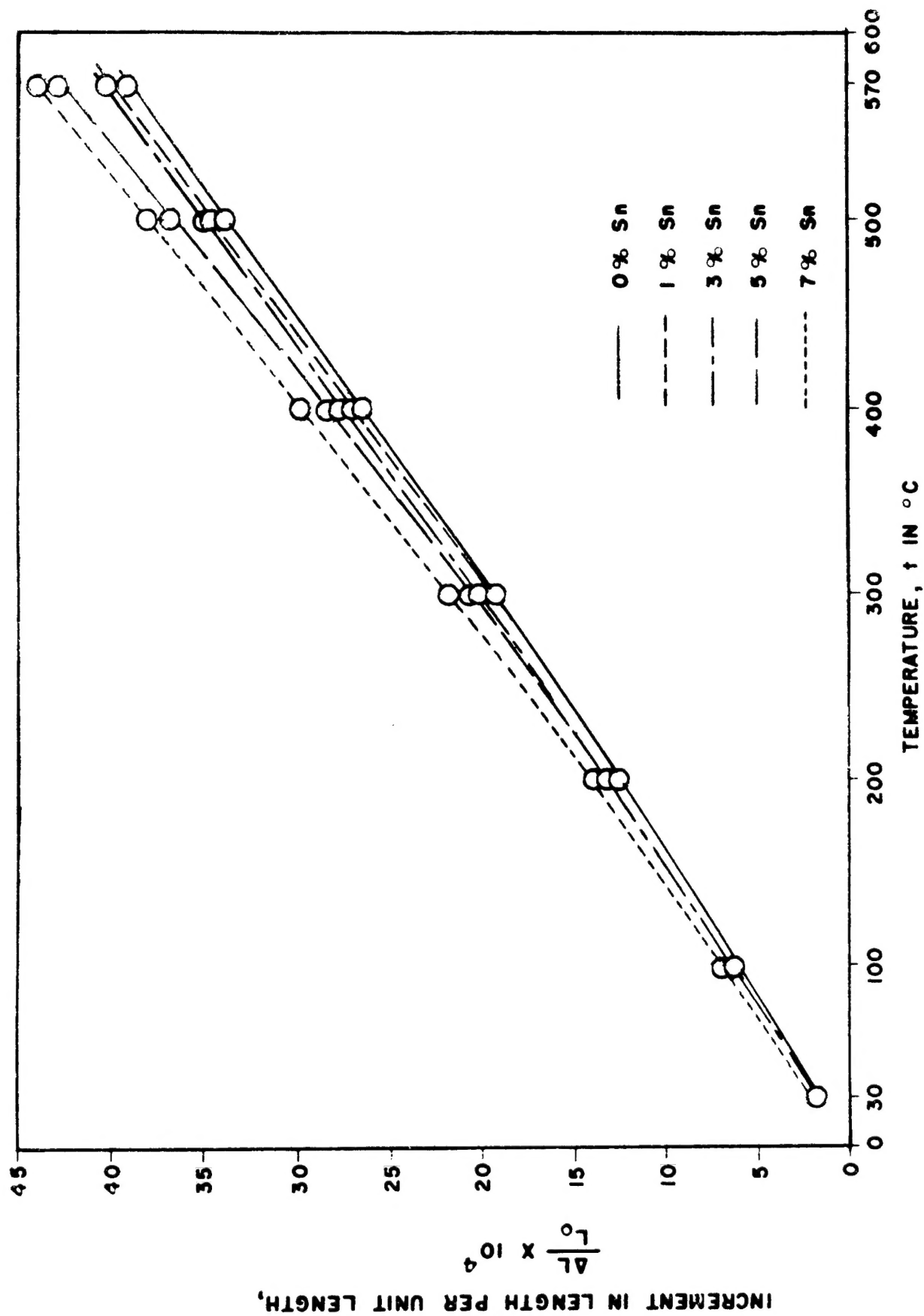
(2) Ibid., p. 35.

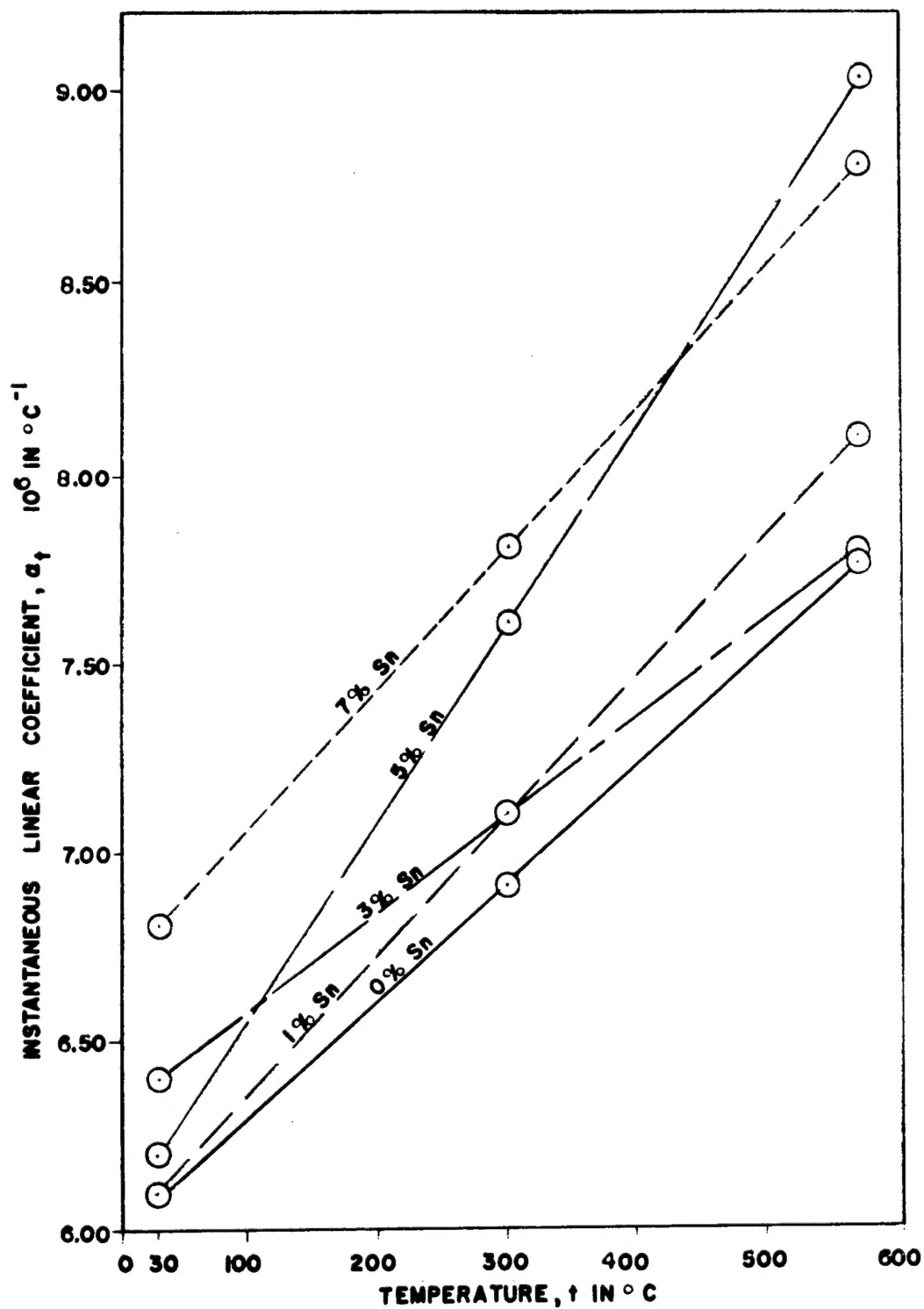Fig. 1 Linear thermal expansion of zirconium and zirconium-tin alloys.
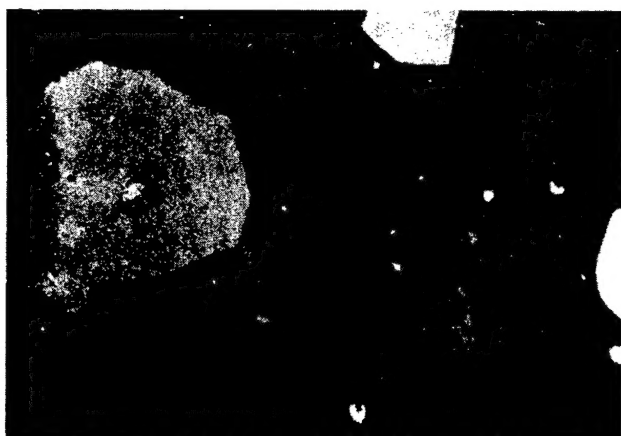
Fig. 2 Variation of instantaneous linear thermal coefficient of expansion of zirconium and zirconium-tin alloys with temperature.

(a)

(b)

(c)

(d)

(e)

Fig. 3 Photomicrographs of Zirconium and Zirconium-Tin Alloys.
Polarized Light. 200X